

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:)	
Toshiki MAEDA)	Group Art Unit: 1795
Application No.: 10/715,525)	Examiner: Jane J. Rhee
Filed: November 19, 2003)	Confirmation No. 4709
For: ACTIVE MATERIAL FOR)	
POSITIVE ELECTRODE OF)	
LITHIUM SECONDARY BATTERY))	

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

DECLARATION UNDER 37 C.F.R. § 1.132

I, Ryuichi KUZUO, do hereby make the following declaration:

1. I am a Japanese Citizen, residing at 17-3, Isoura-cho, Niihama-shi, Ehime-ken, Japan.
2. I have been awarded a Doctor of Science from Tohoku University, Japan.
3. I have been employed by Sumitomo Metal Mining Co., and its predecessor corporation since April 1, 1986, and I am presently Manager of Development Section of the Battery Materials Department. During my employment at Sumitomo Metal Mining Co., I have been with the Advanced Materials Division, Isoura Plant.
4. I have read and understand the rejections presented in the Final Office Action mailed October 14, 2009, in U.S. Patent Application No. 10/715,525, and the reference cited therein, EP 0 944 125 A1. In my opinion, a person of ordinary skill in the art of an active material for a positive electrode of a lithium

secondary battery would recognize that EP 0 944 125 A1 does not disclose a lithium-nickel composite oxide that inherently possesses a Li site occupancy rate of 98% or greater, and an average particle size of spherical secondary particles ranges from 5 μm to 15 μm , and a difference between the specific surface area before and after a washing process for assessing characteristics is 1.07 m^2/g or less.

5. Given my education and experience, particularly in the area of battery compositions and manufacturing, I consider myself able to provide the following testimony regarding the knowledge of one of ordinary skill in the art regarding certain lithium ion battery technology, as well as the following experiments conducted by me or under my supervision.

6. Purpose of Experimentation

To verify that the characteristics of the lithium composite oxides of the present invention are not obtainable by a manufacturing method disclosed in Sunagawa et al. (EP 0 944 125 A1), the lithium composite oxides of A11, A12, A16 and A21 of Experiment 2 listed in Paragraph 0033, Table 2, which are manufactured according to the manufacturing method and under the conditions disclosed in the specification of Sunagawa et al., and the Li site occupancy rate and difference in specific surface area are measured based on the measurement method of the present invention.

7. Experimentation

[Experiment 1]

Lithium hydroxide, nickel hydroxide, cobalt hydroxide and aluminum hydroxide were mixed in a mortar so that the atomic ratio of Li: Ni: Co: Al became 1.0: 0.6: 0.3: 0.1, then under an oxygen atmosphere, was fired for 20 hours at 750 $^{\circ}\text{C}$, to obtain a lithium composite oxide. The obtained composite oxide was an aggregate block, so the aggregate block was pulverized using a jet mill to form a composite oxide powder. The obtained composite oxide was then measured using a laser diffraction particle size analyzer (Nikkiso Co., Ltd., Microtrac), and it was found that the median size was 7.8 μm , with the amount containing particles having a particle size of 1 μm or less was 7.7%. Moreover, the specific surface area of this powder was measured using a specific surface area measurement apparatus that employs the nitrogen adsorption method (Yuasa-Ionics Inc., Quantasorb QS-10), and it was found that the specific surface area was 1.02 m^2/g .

The powder X-ray diffraction pattern of the obtained composite oxide was measured using an X-ray diffraction apparatus that uses Cu-K α rays (Rigaku Corporation, RAD-rVB), and it could be confirmed that the composite oxide was the cathode active material having layered hexagonal crystal structure. Also, from Rietveld analysis of the X-ray diffraction pattern, the Li site occupancy rate of the 3a site was found to be 96.2%. In addition, in order to evaluate this composite oxide, 20g of the composite oxide powder and 500g of water were placed into a beaker and stirred for 1 minute using a stirrer at a temperature of 25 °C. After that, the slurry was passed through a filter, and the obtained precipitate was processed for 24 hours at 150 °C in a vacuum drier to obtain dry powder. The specific surface area of the dry powder obtained after washing was measured and found to be 2.22 m²/g.

[Experiment 2]

Except for mixing Lithium hydroxide, nickel hydroxide, cobalt hydroxide and titanium hydroxide in a mortar so that the atomic ratio of Li: Ni: Co: Ti became 1.0: 0.6: 0.3: 0.1, the experiment was performed in the same way as that of Experiment 1 to obtain a Lithium composite oxide. The obtained composite oxide had a median size of 7.5 μ m, the amount containing particles having a particle size of 1 μ m was 7.2%, and the specific surface area was 1.12 m²/g. The Li site occupancy rate at the 3a site was found in the same way as in Experiment 1, and was found to be 96.6%. Moreover, in order to evaluate this composite oxide, the composite oxide was washed as in Experiment 1, then the specific surface area of the dry powder was measured and found to be 2.47 m²/g.

[Experiment 3]

Except for mixing Lithium hydroxide, nickel hydroxide, cobalt hydroxide and zinc hydroxide in a mortar so that the atomic ratio of Li: Ni: Co: Zn became 1.0: 0.6: 0.3: 0.1, the experiment was performed in the same way as that of Experiment 1 to obtain a Lithium composite oxide. The obtained composite oxide had a median size of 8.1 μ m, the amount containing particles having a particle size of 1 μ m was 6.2%, and the specific surface area was 1.02 m²/g. The Li site occupancy rate at the 3a site was found in the same way as in Experiment 1, and was found to be 96.4%. Moreover, in order to evaluate this composite oxide, the composite oxide

was washed as in Experiment 1, then the specific surface area of the dry powder was measured and found to be 2.36 m²/g.

[Experiment 4]

Except for mixing Lithium hydroxide, nickel hydroxide, cobalt hydroxide and magnesium hydroxide in a mortar so that the atomic ratio of Li: Ni: Co: Mg became 1.0: 0.6: 0.3: 0.1, the experiment was performed in the same way as that of Experiment 1 to obtain a Lithium composite oxide. The obtained composite oxide had a median size of 6.9 μm , the amount containing particles having a particle size of 1 μm was 8.2%, and the specific surface area was 1.21 m²/g. The Li site occupancy rate at the 3a site was found in the same way as in Experiment 1, and was found to be 97.0%. Moreover, in order to evaluate this composite oxide, the composite oxide was washed as in Experiment 1, then the specific surface area of the dry powder was measured and found to be 2.46 m²/g.

M	Specific surface area before washing (m ² /g)	Specific surface area after washing (m ² /g)	Difference between the specific surface area before and after washing (m ² /g)	Li site occupancy rate (%)
Al	1.02	2.22	1.20	96.2
Ti	1.12	2.47	1.35	96.6
Zn	1.02	2.36	1.34	96.4
Mg	1.21	2.46	1.25	97.0

8. Conclusion

In the present invention, as raw material, used is spherical powder of cobalt-nickel composite hydroxide to which metallic element M is added and having an average particle size of approximately 10 μm , and lithium hydroxide is mixed with the above raw material, and the obtained mixture is fired to obtain a spherical lithium-nickel composite oxide. This lithium-nickel composite oxide is formed into spherical secondary particles formed by agglutination of many of the primary particles. Therefore, the lithium-nickel composite oxide is characterized in that the specific surface area thereof is 0.5 to 0.9 m²/g, which is not so large, and even after washing test the shape of the spherical secondary particles is maintained,

so the change in the specific surface area is $1.07 \text{ m}^2/\text{g}$ or less, which is not a large difference.

On the other hand, when combined according to the method based on the examples of Sunagawa et al., as was shown in the present experiments, the specific surface area of the obtained lithium-nickel composite oxide was a large $1.02 \text{ m}^2/\text{g}$ or greater. The reason for this is thought to be due to the fact that the raw materials cobalt, nickel and metallic element M are mixed in a mortar such that each is solutionized plenty and uniformly on the atomic level, and then after being fired, are pulverized to a very fine primary particle level using a jet mill. Many of the primary particles have a size of $1 \text{ }\mu\text{m}$ or less, however, a few or several tens of primary particles come together and form an aggregate clump, so the average particle size measured by a grain size distribution device was several μm . The aggregate state largely depends on the pulverizing conditions of the jet mill, and it also depends on the sintering conditions because the aggregate occurs with sinter, and therefore in the active material of Sunagawa et al., by washing this aggregate clump, the aggregate is broken up and the primary particles become separated. Whether or not the secondary particles are broken up to become primary particles is largely influenced by the aforementioned manufacturing conditions.

Particularly, when lithium and the other metal elements are combined such that the total molar ratio becomes 1.0:1.0 as in the examples of Sunagawa et al., there is not much excess lithium so the bond strength of the aggregate is weak, and, due to this, the aggregate clump further easily breaks up by washing. The primary particles become separated, and by the exposing the surface, the specific surface area further increases. Therefore, the difference in the specific surface area before washing and after washing becomes extremely large. It is not possible to keep the difference in the specific surface area at $1.07 \text{ m}^2/\text{g}$ or less as asserted in the present invention.

Moreover, because the total molar ratio of the lithium and the other metallic elements is 1.0:1.0, the Li site occupancy rate reaches a maximum at 97.0%, and it is not possible to achieve the Li site occupancy rate of 98.0% or greater as asserted in the present invention.

9. I declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated: March 11, 2010

By: Ryuichi Kuzuo
Ryuichi KUZUO